# CONJUGATED POLYMER SENSORS: DESIGN PRINCIPLES TOWARDS ENHANCED VERSATILITY

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## ABSTRACT

A description of how semiconducting fluorescent polymers function as chemosensors for a variety of chemical vapors is presented. Amplification is achieved by transport of optically induced excitations throughout a polymer film. Careful and thoughtful design of polymer chemical structures is crucial to achieving high sensitivity towards nitroaromatic explosives such as trinitrotoluene (TNT) and dinitrotoluene (DNT). These semiconductive materials have been incorporated into functional sensory devices used for ultratrace explosive detection in the search for hidden landmines. Research efforts in our group have been aimed improving the sensitivity, selectivity, and versatility of conjugated polymer sensors through rational molecular design.

## 1. INTRODUCTION

A conjugated polymer is defined as a macromolecule in which the entire main chain is bound together not only by saturated sigma bonds, but also by a continuous pattern of unsaturated, conjugated pi bonds. This electronic conjugation between each repeat unit creates a "molecular wire". The resultant coalescing of molecular orbitals creates a semiconductor band structure, including a valence band (filled with electrons) and a conduction band (devoid of electrons). The semiconducting nature of organic conjugated polymers gives them interesting and useful optical and optoelectronic properties.

The ability of synthetic chemists to vary the chemical structures of polymerization monomers allows for the design and tuning of conjugated polymers for particular applications. One of the applications for which fluorescent conjugated polymers have found a particularly promising future is in chemical sensors (McQuade, Pullen, and Swager, 2000). They have the ability to self-amplify their fluorescence quenching response to the binding of explosive nitroaromatic molecules such as TNT or DNT (Yang and Swager, 1998).

The detection of explosives and ordinances is a problem researchers from many scientific fields have been addressing for years. Nevertheless, undetected explosives, in a variety of settings, remain a major security concern. Especially challenging is the detection of explosives, such as landmines, in uncontrolled environments such as battlefields. The highly variable environmental conditions present in such locations can present interferences for detector technologies in the form of fluctuating temperature, humidity, light, wind, and soil. These complications, along with the low vapor pressure of explosives like TNT, dictate that only a very sensitive and robust technology will give reliable results to the soldier in the field. Conjugated polymer sensors, because of their self-amplifying characteristics and tunability, are extraordinarily effective for the detection of nitroaromatic explosives.

## 2. AMPLIFIED FLUORESCENT POLYMERS (AFPs)

### 2.1 Energy Migration and Amplification

The band diagram of a conjugated polymer in Fig. 1 illustrates how the exciton transport properties of semiconducting fluorescent organic materials give rise to large amplifications for explosive detection (Zhou and Swager, 1995). A photon of energy $h\nu$ is absorbed by the material, which promotes an electron from the valence (filled) band of the semiconductor to the conduction (empty) band. The resulting electron-hole pair (exciton) is bound together as a "quasi-particle". The conjugated nature of the material allows the exciton to migrate throughout the polymer. In this fashion, the exciton "samples" many potential binding sites within its lifetime (typically on the order of one nanosecond). If the exciton interacts with a binding site to which TNT is bound, its fluorescence (emission from the excited state to the ground state) is quenched. This situation can be compared to a string of light bulbs that are wired in series, in which the failure of just one bulb causes the entire string to be extinguished.

Whereas complete fluorescence quenching would be observed in the situation Fig. 1 depicts, only a small percentage of quenching would be observed in the scenario illustrated in Fig. 2., in which individual, non-conjugated binding sites are exposed to the same concentration of TNT. This is because each exciton is confined to its particular molecule and can only sample one binding site. Therefore, emission is observed from those molecules to which TNT is not bound, and a much weaker signal

# Report Documentation Page

*Form Approved*
*OMB No. 0704-0188*

| | | |
|---|---|---|
| 1. REPORT DATE<br>**00 DEC 2004** | 2. REPORT TYPE<br>**N/A** | 3. DATES COVERED<br>**-** |

4. TITLE AND SUBTITLE
**Conjugated Polymer Sensors: Design Principles Towards Enhanced Versatility**

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
**W. Thomas III* and T. M. Swager Department of Chemistry Massachusetts Institute of Technology Cambridge, MA, 02139**

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
**Approved for public release, distribution unlimited**

13. SUPPLEMENTARY NOTES
**See also ADM001736, Proceedings for the Army Science Conference (24th) Held on 29 November - 2 December 2005 in Orlando, Florida. , The original document contains color images.**

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT<br>**unclassified** | b. ABSTRACT<br>**unclassified** | c. THIS PAGE<br>**unclassified** | **UU** | **6** | |

**Standard Form 298 (Rev. 8-98)**
Prescribed by ANSI Std Z39-18

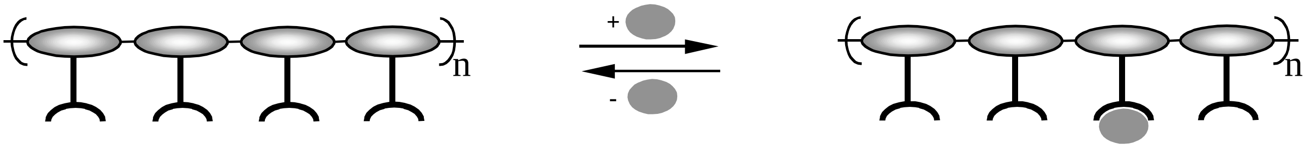


Fig. 1: Conjugated polymer "molecular wire" interacting with a small concentration of TNT quencher. This scenario would give complete fluorescence quenching of the polymer chain.

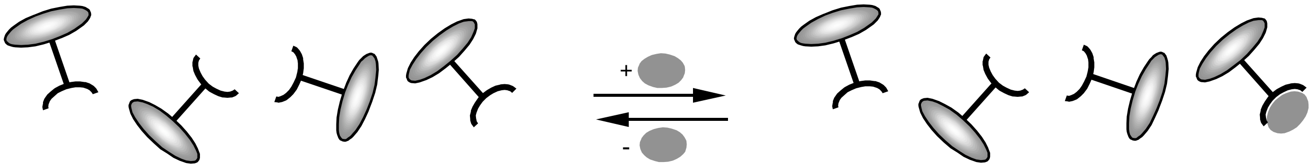


Fig. 2: Collection of individual receptor-chomophore molecules exposed to a small concentration of TNT quencher. This scenario would only give 25% quenching of the sample.

(fluorescence quenching) is recorded for the same concentration of explosive. This general approach of chemosensing via amplified fluorescence quenching was first demonstrated using a poly(phenylene-ethynylene) containing cyclophane-based receptors with paraquat as an analyte. It was found that the exciton could sample about 130 of the individual phenylene ethyne units during a one-dimensional random walk along the polymeric backbone (Zhou and Swager, 1995).

## 2.2 Fluorescence Quenching By Photoinduced Electron Transfer

It is the amplifying abilities of conjugated polymer sensors that make them so unique and effective. Nevertheless, there must be a signal present that can be amplified for this scheme to be effective. Even if an infinite number of binding sites could be sampled, it would be of no use if the bound analyte could not alter the emission of the polymer. Although there are several potential mechanisms by which an analyte can alter the emission of a conjugated polymer, photoinduced electron transfer fluorescence quenching (PICT) is the most effective. A basic band diagram illustrating how PICT works is depicted in Fig. 3. The valence band (VB) and conduction band (CB) of the polymer are shown, as is the lowest unoccupied molecular orbital (LUMO) of TNT. Irradiation of the polymer with a photon causes promotion of an electron to the CB, which is now of a much higher energy. The low-lying LUMO of TNT can then, in an exergonic process, accept the electron from the excited state of the polymer. This in effect destroys the polymer-based excited state, and as a result the polymer can no longer fluoresce. The final step of reverse electron transfer from TNT's LUMO to the polymer VB is a non-radiative process.

If the energy of TNT's LUMO was not below the CB

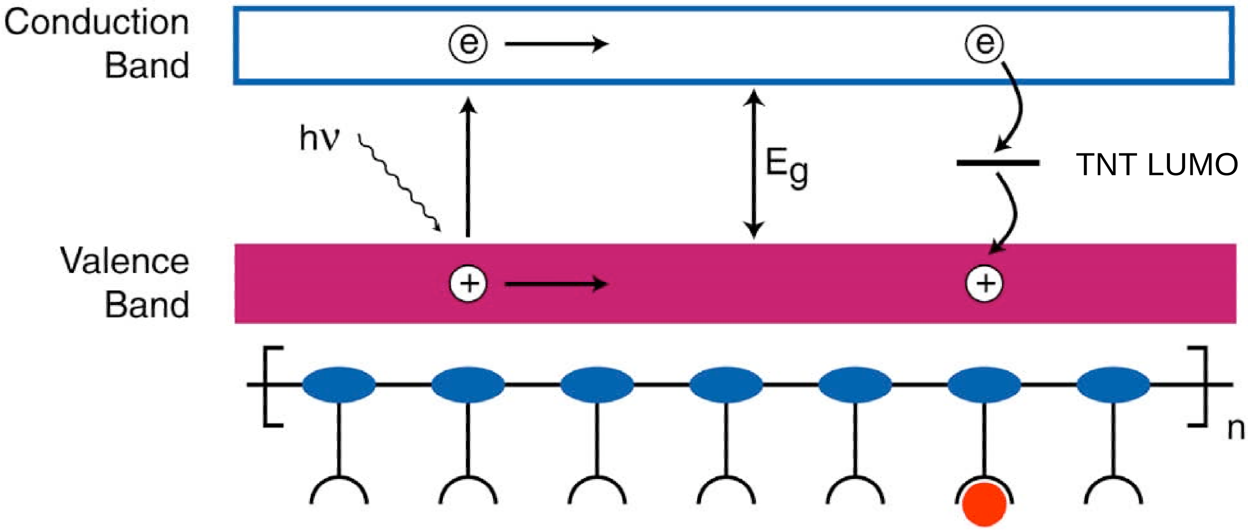


Fig. 3: Band diagram illustrating exciton transport and electron transfer fluorescence quenching.

of the conjugated polymer, electron transfer would not have been energetically favorable and fluorescence quenching could not have taken place. This qualitative observation can be defined more precisely as Eq. (1) (Yanagidate, et al., 1993).

$$\Delta G(\mathrm{et}) = E_{ox}(\mathrm{D}) - E_{red}(\mathrm{A}) - E_{ex}(0,0) - \lambda \qquad (1)$$

$\Delta G$ here represents the driving force of the photoinduced electron transfer reaction, while $E_{ox}(D)$ and $E_{red}(A)$ refer to the oxidation potential of the electron donor (conjugated polymer) and the reduction potential of the acceptor (TNT, -0.7 eV versus standard calomel electrode [SCE]), respectively. $\lambda$ refers to the solvation-induced stabilization of the highly charged ion-radical pair that is the product of the electron transfer reaction. This varies from solvent to solvent and correlates with the dielectric constant of the medium. $E_{ex}(0,0)$ stands for the energy associated with the transition of an electron from the CB to the VB in the fluorescent polymer. It is this photoexcitation energy that most often allows the electron transfer reaction to be energetically favorable.

This relationship also conveys one of the reasons why the sensing of explosives can be so effective with this method. Most explosives, especially TNT and other nitroaromatic compounds, are highly electron deficient and have favorable reduction potentials. For instance, the reduction potential of TNT and DNT are only -0.7 V and –1.0 V (vs. SCE) respectively, quite favorable when compared with other potential electron acceptors, such as 1,4-dicyanobenzene (-1.7 V vs. SCE). This means that if the sensory material emits light, for example, at 460 nm, the oxidation potential of the sensing polymer can approach close to 2.0 V vs. SCE and still give a negative change in free energy for photoinduced electron transfer, theoretically allowing for amplified fluorescence quenching and detection of TNT.

## 3. SOLID-STATE AFP CHEMOSENSORS

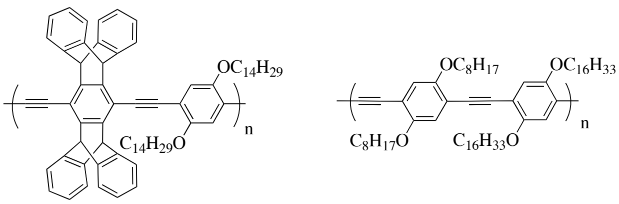
### 3.1 Potential s and Pitfalls

Although the first demonstrations of the utility of AFPs for highly sensitive detection were in solution, these amplifications represent only the lowest limit of what these systems can offer. This is because when the polymer chains are isolated and cannot communicate, excitons are forced into a one-dimensional random walk during which excitons retrace the same segments of the polymer chain multiple times. According to this model, the amplification factor of 130 requires that excitons make $130^2$ hops, which represents an efficiency (number of productive hops) of less than 1%. In addition, explosive detection sensitivity using a solution-based AFP sensor is often limited by the rate of diffusion of the polymer and the analyte. Achieving strong solution-state static binding is especially difficult because of competitive solvation of the analyte and polymer molecules. Also, a solution-state sensor would require frequent and cumbersome handling of toxic solvents and careful solution preparation.

On the other hand, the ability to produce a thin film conjugated polymer sensor brings many potential advantages. It simplifies the operation of a sensory device for soldiers in the field, as well as eliminating competitive solvation of analyte molecules and the accompanying limitation of the diffusion rate. Most importantly, this extends the dimensionality of the amplification from one dimension to two or three dimensions. Having the polymer chains in a thin film allows excitons to not only travel along one polymer chain, but to also “jump” to other nearby chains. Therefore, excitons execute a multidimensional random walk, limiting the number of unproductive “retracing” steps taken and further increasing the amplification (Levisky, Kim, and Swager, 1999). This brings the amplification factor in a simple, unoptimized polymer film closer to 17,000 times that of a single, isolated chromophore-receptor combination.

There are clearly many advantages to operating a conjugated polymer as a solid polymer film. There are, however, serious complications that can arise upon making thin films of conjugated polymers. The structural nature of the rigid rod-type polymers forces them into a highly planarized geometry. In the solid state, this structural feature often induces aggregate formation, in which the planar chains stack on each other with pi-orbitals from adjacent chains interacting. These types of interactions create local energy minima in the potential energy surface of the film. When this effect is combined with the efficient intra- and inter-chain exciton migration in AFP thin films, the result is that a large amount of the initial excitation energy is funneled to aggregate sites. Conjugated polymer aggregates formed from pi-stacking are usually only very weakly emissive (Jenekhe and Osaheni, 1994). The resulting weak emission from polymer aggregates means more TNT must be bound for the sensor to give a reliable response, reducing the sensitivity of the device. Also, the extent of exciton migration is restricted because of the low-energy trap sites.

As a result of these potential pitfalls, our designs have centered on avoiding interchain interactions in the solid state. These efforts have focused on attaching large and rigid pendant groups onto conjugated polymer backbones in order to prevent the polymer chains from coming so close in the thin film as to form aggregates. A particularly useful structural moiety is the pentiptycene unit, which polymer **1** in Fig. 4 contains (Yang and Swager, 1998). This rigid three-dimensional structure not only prevents severe fluorescence quenching in the solid



**1** **2**

Fig. 4: Structures of AFPs **1** and **2**.

state, but also by keeping the chains apart, reduces photochemically induced intermolecular interactions that can lead to photobleaching and degredation of the material (Williams and Swager, 2000). As a result, **1** is a highly stable sensory material with strong solid state emission.

### 3.2 Important Parameters for Solid-State Fluoresence Quenching

Fig. 5 shows the fluorescence response of a film of **1** as a function of exposure time to TNT equilibrium vapor pressure (Yang and Swager, 1998). The dimunition of the polymer's fluorescence intensity in response to the presence of TNT vapor is very efficient. After only a matter of seconds, significant fluorescence quenching is observed. This sensitivity is primarily derived from the exciton transport properties of conjugated polymers that were previously described. However, more is required of a conjugated polymer sensor than simple amplilfication. There are several other factors that help determine the efficiency of vapor phase detection by fluorescence quenching (FQ). These are the vapor pressure of the analyte (VP), the binding constant of the analyte ($K_b$), and the rate of photoinduced electron transfer, which depends strongly on the reaction driving force, previously described in Eq. (1). The relationship of fluorescence quenching efficiency to these parameters can be simply summarized in Eq. (2).

$$\mathrm{FQ} \propto (K_b)[\exp(-\Delta G_{et})^2](\mathrm{VP}) \qquad (2)$$

As previously illustrated, the photoinduced electron transfer reaction must be energetically favorable in order to induce quenching of the polymer film's emission by nitroaromatics such as TNT or DNT. Using Eq. (1), along with the redox and optical properties of polymer **1** shows that the PICT reaction with this system has a driving force ($-\Delta G$) of 0.82 eV for TNT and 0.52 eV DNT. Note that in the solid state there is no solvent reorganization energy ($\lambda$) to assist in the stabilization of the ion pair.

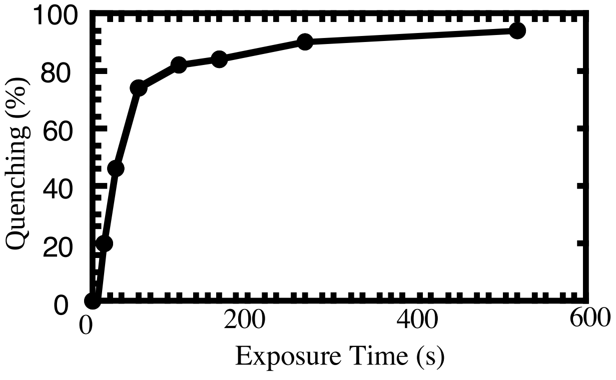


Fig. 5: Temporal response of AFP **1** to an equilibrium vapor pressure of TNT.

As a compliment to the strong driving force for reduction of nitroaromatics like TNT, this energetic relationship also builds selectivity into the sensory scheme. Only molecules that have a very favorable reduction potential will quench the polymer's fluorescence. According to Equation (1), only if the reduction potential of the analyte is greater than –1.52 eV will there be a negative free energy change for quenching. This leaves only a very small family of molecules, basically limited to nitroaromatics and quinones. Even benzophenone, 1,4-dicyanobenzene, and 1,4-dichlorobenzene, all relatively strong electron acceptors on an absolute scale, do not quench the emission of **1**.

The binding constant ($K_b$) is also an important parameter for solid state fluorescence quenching. If the analyte of interest does not interact with the polymer film, then the electron transfer reaction (which requires intimate contact between electron donor and acceptor) cannot occur. TNT and DNT are uniquely suited to bind to polymers such as **1**. These analytes are very planar, aromatic, and have multiple fully conjugated, strongly electron withdrawing nitro groups. This gives TNT and DNT strong pi-acid properties, meaning that the electron affinity of the pi systems of these molecules is very large. As a result, TNT and DNT form strong ground state complexes through stacking of pi-systems. This interaction is based on electrostatic attraction between the strongly pi-acidic nitroaromatics and the moderately electron rich aromatic systems in **1**.

**1** also displays size-exclusion properties. Diffusion of the TNT or DNT into the bulk of the film is necessary to achieving an efficient quenching response. If the analyte is not able to diffuse into the majority of the polymer film, then only quenching from the surface of the film can be observed, limiting the sensitivity of the material. The rigid, three-dimensional structure defined by the pentiptycene groups allows for the formation of galleries capable of inducing the binding of small, flat nitroaromatics, while larger and more three-dimensional interferents are excluded. This concept is illustrated in Fig. 6. It might seem reasonable to hypothesize that polymer **2**, which contains more electron donating groups per repeat unit would be more sensitive to TNT vapor than **1** because of a larger electrostatic attraction. Polymer **1**, however, is much more sensitive to TNT vapor. This is attributed to the aforementioned porosity present in thin films of **1**. This "internal free volume" that is presented by iptycene groups is an extraordinarily useful aspect of this structural moiety.

To further enhance binding selectivity, polymer **3**, which incorporates polycyclic aromatic groups that have triphenylene residues. These structures present three-fold symmetric sites that are complementary to the positive charge on TNT and DNT. This effect is depicted in Fig. 7, for which electrostatic potentials have been calculated for TNT and the triphenylene segment of **3**. **3** therefore exhibits improved sensitivity to TNT vapor.

In summary, there are many important factors that must be considered when designing and synthesizing a conjugated polymer sensor. Not only must the PICT process be exergonic for fluorescence quenching to be possible, but solid-state aggregation of polymer films must also be minimized in order to maximize sensitivity and reproducibility of results. A strong binding of the analyte of interest is also critical, which is facilitated in these cases by the pi-acidic properties of TNT and DNT, as well as the electrostatic and porous properties of polymers such as **1** and **3**. These systems embody an excellent balance of all these necessary properties for nitroaromatic analytes, and as a result are highly specific and sensitive sensory materials for TNT and DNT vapor.

## 4. AFP DEVICES – TNT DETECTION IN THE FIELD

As is the case for any technology for the detection of explosives, the true test of merit is how it performs as part of an operable device in the field. This technology affords excellent laboratory results as described above. Taking it into the field, however, imposes many potential complications. Using polymers developed in our research group, Nomadics Inc. (www.Nomadics.com) has built a series of completely portable instruments, under the trade name Fido, with femtogram detection limits of TNT (Cumming, Fisher, and Sikes, 2004).

This detection limit greatly exceeds other detection technologies, and in side-by-side comparisons these devices shows sensitivity comparable to trained canines in field tests for the detection of buried land mines. The remarkable sensitivity of this technique is sufficient to overcome both the low vapor pressure of TNT (ppb range) and the fact that the concentration of TNT in the air over a buried landmine is often several orders of magnitude lower than the equilibrium vapor concentration. In addition, the selectivity inherent in using this method with well-designed polymers such as **1** and **3** is very important. The battlefield areas in which land mines and other explosives are deployed are contaminated with hundreds of chemicals that are not encountered in a laboratory environment, and relatively unselective technologies such as metal detectors bring about a high probability of time-consuming false alarms. Use of these AFP devices also avoids the expensive and time consuming process of training dogs as well as the feeding and caring for live animals.

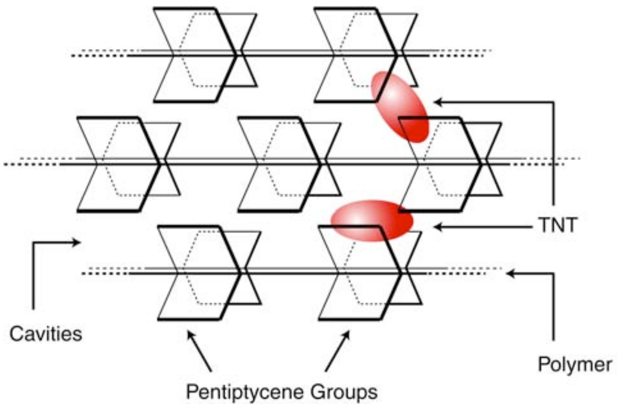
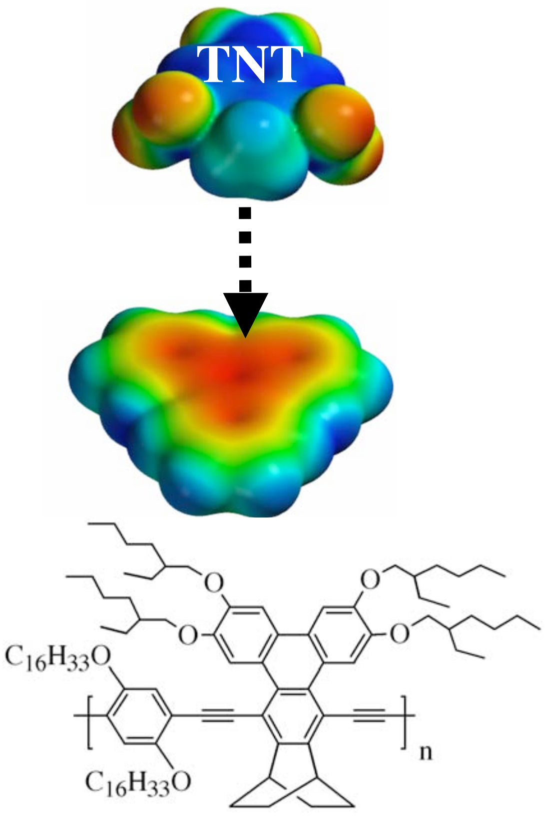


Fig. 6: Conceptual illustration of how the rigid pentiptycene groups in polymer **1** induce porosity in the thin film and allow TNT to diffuse into the film.



**3**

Fig. 7: Triphenylene-containing polymer **3** below an illustration of the electrostatic match between TNT and triphenylene.

Also, the stability of well-designed polymer films has been critical to the success of these devices in field tests. The complex environment of a battlefield location can present challenges such as changes in temperature and humidity. The AFP used must be photochemically stable conditions for long periods of time under these potentially extreme conditions. Whereas most conjugated polymers readily photobleach over even short durations under ambient conditions, well-engineered polymers such as **1** give consistent fluorescence intensities even after long periods of irradiation in field tests. This is attributed to the pentiptycene moieties forming a protective sheath around the polymer backbone, serving to insulate it and prevent intermolecular photochemical reactions and self-quenching. As a result, these devices are stable and operable even under extreme environmental conditions.

The simplicity of using an optical signal such as fluorescence allows for the fabrication of portable and easily operable devices. The inherent sensitivity and selectivity of this technique has led to their successful application to explosive detection in a variety of field test situations, including the searching of personnel, vehicles, large areas of land, and even underwater. Most recently, these devices have been taken beyond field tests and are being evaluated by soldiers for the detection of hidden explosives in truly dangerous situations.

## CONCLUSIONS

Research in explosive detection is highly applicable in many settings, from homeland security to protection of the warfighter. Explosive detection using fluorescence quenching of amplified fluorescent semiconducting conjugated polymers is an extremely effective technique that can supply high sensitivity and selectivity for vapor phase nitroaromatic explosives. The “molecular wire” approach to signal amplification affords very high sensitivity by allowing one sensing exciton to sample many potential binding sites within its excited state lifetime. Taking materials such as **1** into the solid state is necessary for achieving maximum sensitivity and allows for the fabrication of operable devices that exhibit high performance in complex environments. This performance is due to exceptional durability, as well as the sensitivity and selectivity of these polymeric materials towards vapors of nitroaromatic explosives. Their ongoing evaluation by soldiers on the battlefield demonstrates their potential impact on warfighters in the future.

Rational molecular design is the cornerstone of this research. Many issues and complications, such as those described above, must be considered in order to create an effective and reliable sensory material for a targeted analyte such as TNT. The effectiveness and applicability of these types of materials is constantly being improved by research in both industry and academia. Ongoing research on our laboratory is targeting the detection of other explosives, including RDX and PETN. With the nearly infinite amount of additional design features and modifications that can be incorporated into the chemical structures of AFP sensory materials, the expansion and improvement of the sensitivity, selectivity, and versatility of this technique is an exciting and important goal.

## REFERENCES

Cumming, C.; Fisher, M.; Sikes, J., 2004: Amplifying Fluorescent Polymer Arrays for Chemical Detection of Explosives. *Electronic Noses & Sensors for the Detection of Explosives*, J. W. Gardner and J. Yinon, Eds., Kluwer Academic Publishers, 53-70.

Fisher, M. and Sikes, J., 2004: Detection of Landmines and Other Explosives with an Ultra-Trace Chemical Detector. *Electronic Noses & Sensors for the Detection of Explosives*, J. W. Gardner and J. Yinon, Eds., Kluwer Academic Publishers, 53-70.

Jenekhe, S. and Osaheni, J. A., 1994: Excimers and Exciplexes of Conjugated Polymers. *Science*, **265**, 765-768.

McQuade, D.; Pullen, A. E.; Swager, T. M., 2000: Conjugated Polymer-Based Chemical Sensors. *Chem. Rev.*, **100**, 2537-2574.

Williams, V. E. and Swager, T. M., 2000: Iptycene-Containing Poly(aryleneethynylene)s. *Macromolecules*, **33**, 4069-4073.

Yanagidate, M.; Takayam, K.; Takeuchi, M; Nishimura, J; Shizuka, H., 2993: Molecular Conformation Effects on the Relaxation Processes in the Excited State of Naphthalenophanes. *J. Phys. Chem.*, **97**, 8881.

Yang, J.-S. and Swager, T. M., 1998: Fluorescent Porous Polymer Films as TNT Chemosensors: Electronic and Structural Effects. *J. Am. Chem. Soc.*, **120**, 11864-11873.

Yang, J.-S. and Swager, T. M., 1998: Porous Shape-Persistent Fluorescent Polymer Films: An Approach to TNT Sensory Materials. *J. Am. Chem. Soc.*, **120**, 5321-5322.

Zhou, Q. Z. and Swager, T. M., 1995: Fluorescent Chemosensors Based on Energy Migration in Conjugated Polymers: The Molecular Wire Approach to Increased Sensitivity. *J. Am. Chem. Soc.*, **117**, 12593-12602.